Black glasses, bulk and fibers: Obtaining information in the infrared

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Black Glasses, Bulk and Fibers: Obtaining Information in the Infrared

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Black in the visible but highly transparent in the infrared, the chalcogen-based glasses have reached a maturity which makes them competitive materials for several technological applications related to detection in the mid IR spectral domain. As bulk IR transparent materials they offer an advantage compared to germanium crystals, as they are low cost materials which can be shaped into simple or sophisticated IR lenses by molding. Many efforts have been made to optimize the chemical composition in order to make these glasses very resistant to moisture and oxygen corrosion or devitrification. When drawn into optical fibers with different optical configurations, they represent a new generation of waveguides covering the 3 to 12μm spectral domain and paving the way for the development of temperature, chemical or biochemical sensors. Amongst these possibilities, the remote *in situ* analysis of chemical processes (such as fermentation or reactions carried out under microwave or autoclave conditions) as well *in vivo* analysis of biological tissues, are the most exciting. The use of chalcogen glass fiber tips for scanning near field micro-spectroscopy is also a promising field.

The glass forming ability of chalcogen-like materials has been known for decades, and the prototype material, the arsenic trisulfide As_2S_3 leads to easy glass formation. In this kind of material, built from atoms of similar electronegativity, the bond between the chalcogen S and the pseudo-chalcogen As is essentially covalent and is characterized by a strong overlap of the atomic orbitals, rendering these compounds very stable and resistant to chemical corrosion in general. The field of chalcogenide glasses has been recently reviewed by Elliot[1] and the author of this article[2]. The second important feature concerning these materials is based on the fact that one lone pair of electrons on the As atoms and two lone pairs on the chalcogens S, Se or Te are not engaged in the bond. The energy of this non-bonding level is such that its separation with the upper antibonding level is rather weak, resulting in band gap average values E_g being closed to 2eV, causing these "black" glasses to be opaque in the visible. This intrinsic property is a handicap for the transmission in the short wavelength region and until now the highest transparency observed in the visible corresponds to sulfur-containing glasses that are red or yellow colored. All the Se or Te containing glasses are black, with a bandgap which can be as low as 1eV. This poor transmission in the visible is nevertheless compensated by an IR edge which is shifted towards the long wavelength region in such a way that transparency can extend towards the 18 μm region in glasses containing heavy elements such as Te. Consequently, these vitreous materials exhibit a very high transparency in the mid-IR region in

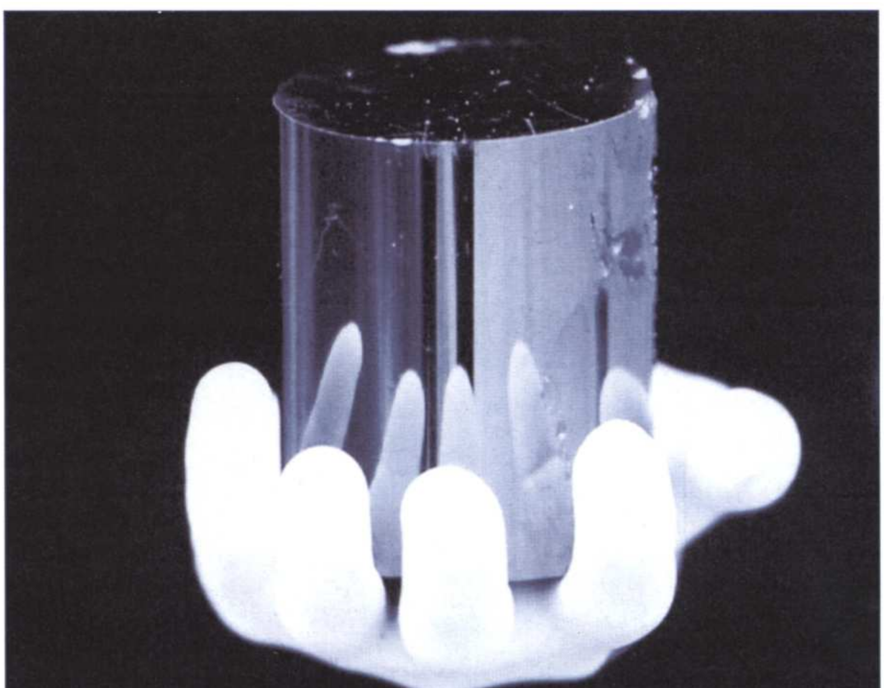

Figure 1. A rod of chalcogenide glass manufactured by the French company Vertex. The material is transparent in the IR range from 1 to 12 μm. Slices of such glass will be molded into asphero-diffractive lenses for IR cameras. Courtesy of CNRS Phototeque: Claude Delhaye photographe.

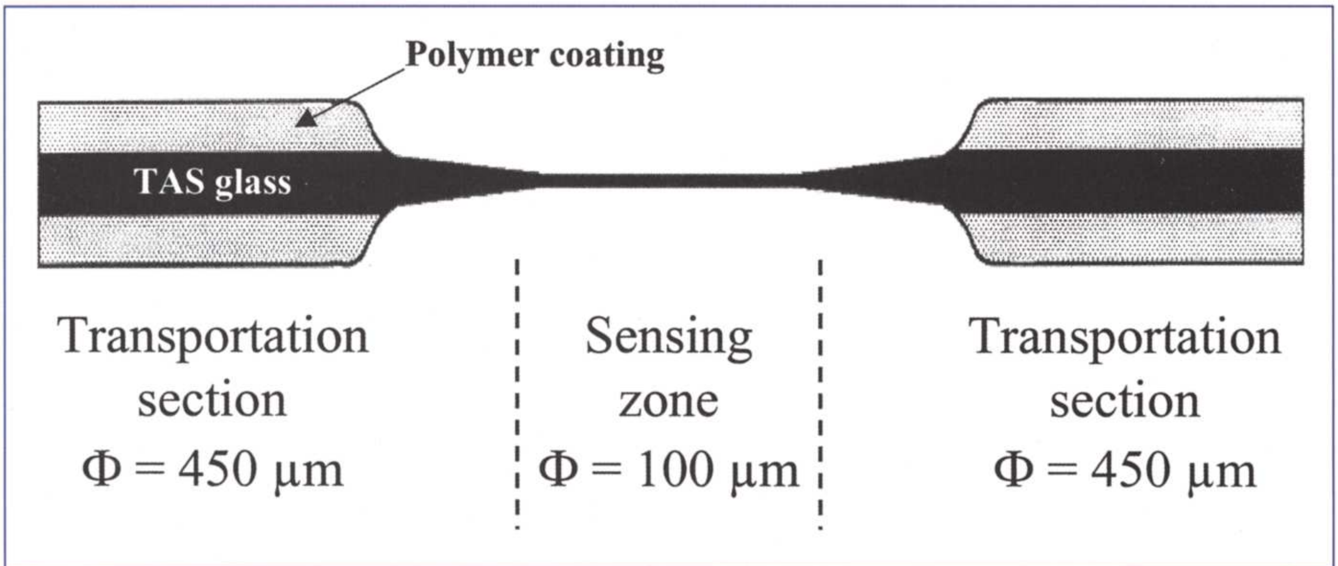

Figure 2. A tapered IR glass fiber used for evanescent wave spectroscopy. The diameter is reduced in changing the drawing speed or by chemical etching in order to increase the amount of the IR light propagating on the surface of the fiber. The glass used for making the fiber is a TAS glass belonging to the Te/As/Se system. In the sensing zone, the polymer coating is eliminated by a solvent.

which are located the strategic optical windows corresponding to the atmospheric transparency (which lie from 3 to 5 μm and 8 to 12 μm). The second window is also of special interest because it corresponds to the room temperature black body emission which is located at around 10 μm. The detection and analysis of IR light has been a strategic military objective for at least two decades, and many night vision systems have been developed, but at a rather expensive cost because they include IR lenses made from germanium. A new generation of optical systems which include molded chalcogenides glasses in their design are now under consideration for low cost thermal imaging. These could be used in infrared cameras for civil and industrial applications (e.g. for assisting firemen or policemen as well as car driving in night or foggy conditions).

The studies of chalcogenide glass compositions that have been published lead to a rather confusing situation. The objective is to select the best glass in terms of resistance to crystallization while keeping an excellent transmission in the 3 to 14 μm window where the oxide-based glasses are opaque. The challenge is to build a floppy covalent framework having the maximum degree of freedom. This would allow bending and rotation of the bonds to produce an aperiodic skeleton, which loses its rigidity when heated up into the liquidus region. The resulting viscous liquid remains out of equilibrium when cooled down to a solid, forming a liquid of infinite viscosity, namely a glass. The building elements used in this framework are related to three kinds of tetrahedral units. The X= S, Se, Te atoms with their two bonding electrons and two lone pairs, the As atom with three bonding electrons and one lone pair and the Ge atoms with its four equivalent sp3 bonds.

Consequently, glasses having different kinds of dimensionality can be produced, ranging from a single dimension chain-like network to 2D or 3D network. Intermediate structural models also exist and these explain the large vitreous domain observed in systems such as Ge/As/X=S, Se. The guide-line used to shift the IR edge is to maximize the number of heavy atoms, but the price to pay for this is weak thermomechanical properties characterized by low glass transition temperatures T_g. When good mechanical characteristics are needed, tetravalent Ge is necessary to increase the dimensionality and rigidity of the glass to the detriment of a part of the IR transparency. On the other hand the glasses exhibiting the most interesting IR edge are Ge-free and belong for example to the Te/As/Se system.

In order to follow the specifications requested by the thermal imaging technology, large pieces of glass with a very homogeneous refractive distribution have to be prepared. Pioneer works in this field have been initiated by Savage[3] and have been conducted on an industrial level by Hilton[4]. Figure 1 shows a sample of glass rod of about 12 cm diameter routinely fabricated by the French company Vertex[5]. If cut into appropriate slices these pieces of chalcogenide glasses can be molded as aspheric and diffractive lenses under moderate temperatures and pressures. This original technology opens the way to low cost IR optical lenses for affordable IR cameras.

When glass compositions are carefully optimized, the selected vitreous material offers exceptional rheological properties which permit optical fiber drawing. The first step consists of the preparation of a high purity glass, produced from purified starting elements, followed by a distillation of the glass liquidus. All the operations are conducted in silica vessels and the final rod preform is obtained after homogenization of the melt and cooling down the silica ampoule with a rigorous temperature program. Fiber preparation from the preform in the drawing tower leads to constant diameters which can be adjusted and modified depending on the drawing speed and the glass temperature. In many applications[6] a regular constant diameter is sufficient, for instance in radiometric devices where the fiber will be used to catch the thermal emission of an object and carry the energy to a MCT IR detector

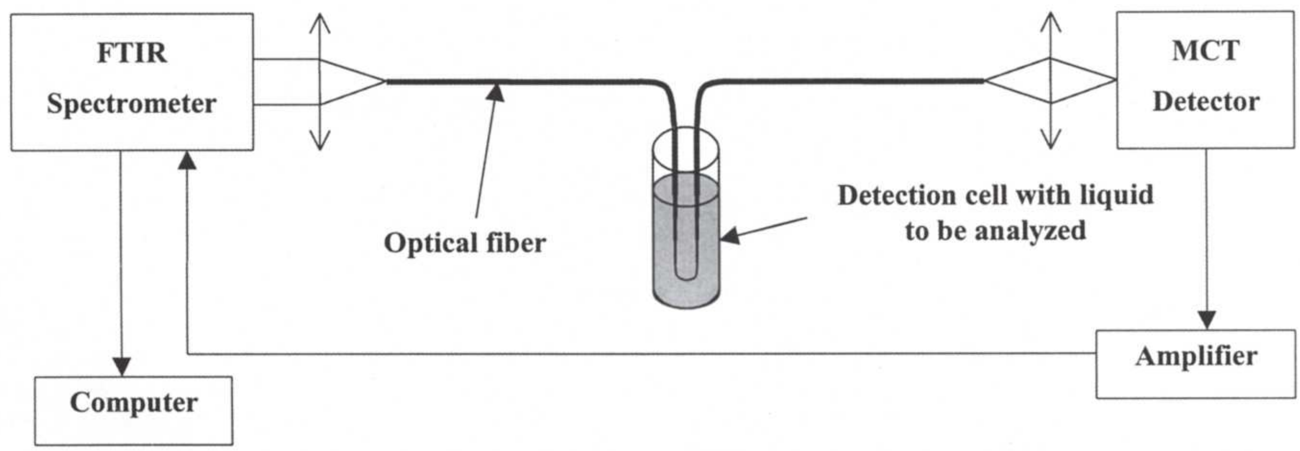

Figure 3. Analytical set-up for IR glass fiber evanescent spectroscopy. The organic material in contact with the surface of the tapered fiber absorbs the evanescent wave IR light and leaves its infrared fingerprints on the detector. This remote IR spectroscopy operates in the 3 to 12 µm range, in which the IR signatures of almost all organic compounds are located.

for temperature measurements[7]. These same kinds of waveguides when coupled with a CO_2 laser can be used to transfer several watts of power towards a target, such as a biological tissue which strongly absorbs the 9,3 µm radiation. That wavelength has been selected because it corresponds to the low loss region of the fiber around 1dB/m, and because of its strong absorption by the tissues.

The optical configuration of the waveguide can also be designed in a completely different way by tapering the fiber over a short distance, say about ten centimeters. This can be achieved either by changing the drawing speed abruptly during the fibering process, or by a chemical etching process using an acidic oxidizing solution which congruently dissolves the glass. Figure 2 represents the result of this tapering operation which, for example, will reduce the fiber diameter from 450 µm in the transportation section, to 100 µm in the tapered sensing zone. Indeed it is well known that when IR light is injected into such a fiber which is transparent from 3 to 12 µm part of the energy travels on the surface of the guide by an evanescent wave or total internal reflection mechanism. This phenomenon increases as the diameter of the waveguide decreases, as verified on calibrated tapered fibers. Figure 3 shows a remote sensing system which includes an FTIR spectrophotometer coupled to an MCT detector via a tapered fiber[8]. When an organic material is put into contact with the sensing zone, it will absorb the IR light propagating on the surface of the fiber and leave its own IR fingerprint on the detector. This novel optical probe called an IR fiber evanescent wave, IRFEW, has been tested and evaluated in several analytical conditions. First of all it has been verified by using alcoholic solutions as a standard that the sensitivity is proportional to the length and inversely proportional to the fiber diameter; concentration as low as 1% can be easily detected. The spectral window covered by this sensor extends from 3 to about 12 µm allowing, for instance, the carbon-halogen vibration detection of Freon or carbon tetrachloride at around 12 µm.

Included in this spectral range are almost all the fundamental vibrations of the organic molecules and of inorganic materials. This favorable situation permits, for instance, *in situ* monitoring of chemical reactions such as the transformation of glucose molecules into alcohol during the invaluable fermentation process leading to wine preparation. Indeed both molecules have IR fingerprints which are different enough to be quantitatively detected. The same analytical methodology has been applied in the milk industry to follow the fermentation of milk into yogurt as characterized by the transformation of lactose into lactic acid. Recently this tapered fiber probe has been tested in a very unusual and hostile situation in the form of a chemical reaction assisted by microwave irradiation. Immersion of the fiber in the microwave oven has permitted researchers for the first time to follow *in situ* the evolution of the different species, giving them valuable information on the reaction mechanism. The same kind of experiment is now in progress under autoclave conditions. The most interesting initiative is the aim of obtaining information on biochemical and biological processes, especially *in vivo* conditions, as permitted by the non- invasive character of this IRFEW remote spectroscopy[9]. The only difficulty lies in establishing a simple mechanical and optical contact between the proteins or tissues to be analyzed and the tapered fiber.

Amongst the crucial targets related to medicine is the early detection of cancer, which is known to be associated with a modification of the conformation of certain proteins which change their structure when the metabolism deregulation starts. It has been demonstrated that the difference between the helix structure of healthy proteins and the tabular structure of malignant tissues is detectable in the mid-IR by examining closely the two IR absorption peaks of the so-called amides 1 and 2 located in the 1650 cm^{-1} region. The same kind of observation has also been noticed by biologists in examining the tissues infected by the prions in the Bovine Spongiform Encephalopathy (BSE) disease.

The sensitivity, compactness and reliability of such optical sensors will significantly improve with the emergence of the new powerful mid-IR sources such as the Quantum Cascade Laser (QCL) which is adjustable to a specific wavelength domain. This optical system will also benefit from the rapid evolution observed in the IR detection technology when bolometers (pyroelectric uncooled detector elements) arrive on the market.

The last emerging domain in which IR fibers are also finding a small niche is due to the need of very sharp fiber tips for scanning near-field IR microscopy. It is possible to apply a chemical etching process to shape these chalcogen based glasses, and very thin and sharp fiber tips have been designed and successfully tested using a free electron laser as an IR source[10].

Although these chalcogenide glasses are not new materials in a strict sense, they appear, like many exotic glasses, to be largely unknown, especially in fields where they may become candidates for technological applications. In the abundant literature, only a few articles promote the understanding and control of the engineering of such materials. Almost nothing is known about phase separation problems, such as microscopic bubble formation during the glass processing. Optical quality requirements impose the control of many rheological and mechanical parameters, which are solved for the moment only by empirical routes. Fundamental work conducted in this author's laboratory indicate, for example, that new composite glass-microcrystal materials called IR vitroceramics will be the next generation of IR transparent materials, either in bulk or fibrous form. Compared to the pure glassy state, for equivalent optical properties, the benefits in terms of thermomechanical properties are unrivalled.

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